

Partitioning and persistence of volatile methylsiloxanes in aquatic environments

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Abstract

The presence of volatile methylsiloxanes (VMS) in the environment has raised concerns among environmental chemists and regulators about their persistence and the risks they may pose to the environment. This thesis explores the partitioning and persistence of VMS in aquatic environments. In **Paper I**, we reported new measurements of the organic carbon/water (K_{OC}) and dissolved organic carbon/water (K_{DOC}) partition ratios of three cyclic volatile methylsiloxanes (cVMS) and of three polychlorinated biphenyls (PCBs), which were used as reference chemicals. We combined new measurements with existing data to construct polyparameter linear free energy relationships (PP-LFER) that describe the K_{OC} and K_{DOC} of diverse sets of chemicals. The findings suggest that cVMS do not conform to single-parameter regressions that relate the chemicals' K_{OC} to their octanol/water partition ratio (K_{OW}). PP-LFERs can accurately describe the K_{OC} and K_{DOC} of cVMS but only if cVMS are included in their training sets. In **Paper II**, we studied the effect of salinity on the K_{OC} and K_{DOC} of three cVMS, two linear volatile methylsiloxanes (lVMS) and three PCBs. We also evaluated the predictive power of the PP-LFERs constructed in Paper I by testing them on the newly measured K_{OC} values of lVMS. The K_{OC} and K_{DOC} increased with increasing salinities similarly to those of the PCBs. PP-LFERs that were trained with datasets that included siloxanes could predict the K_{OC} and K_{DOC} of other siloxanes more accurately than PP-LFERs without siloxanes in the training set. In **Paper III**, we evaluated the effect of temperature on the K_{OC} of VMS and we compared our measurements of the enthalpy of sorption to organic carbon (ΔH_{OC}) to existing measurements of the enthalpy of phase change between octanol and water (ΔH_{OW}). Due to the scarcity of ΔH_{OC} data in the literature it is common practice in modeling calculations to use ΔH_{OW} instead when correcting for temperature changes. The K_{OC} of cVMS increased with decreasing temperatures. Moreover, our results indicate that ΔH_{OC} and ΔH_{OW} may be intrinsically different and hence replacing ΔH_{OC} with ΔH_{OW} in modeling calculations could lead to substantial errors, especially for VMS. In **Paper IV**, we explored the environmental fate of VMS in aquatic environments using multimedia models. In particular, we assessed the differences that may occur in calculations of persistence due to (i) the reported K_{OC} measurements of VMS differing by one log unit (ii) the influence of salinity on K_{OC} , and (iii) the differences in the reported ΔH_{OC} and ΔH_{OW} measurements of VMS. The calculated residence times for decamethylcyclopentasiloxane (D_5) in a site-specific scenario for a Norwegian fjord receiving siloxanes in wastewater ranged from 200 to 1000 days, and demonstrated that the selection of K_{OC} values can result in substantially different calculated persistence. Future partitioning measurements of VMS in the real environment and mass-balance modeling studies in aquatic environments combined with field measurements could help us to deepen our understanding about their persistence and to assess the risks VMS may pose to the environment.

Keywords: *siloxanes, organic carbon, sediment, partitioning, persistence.*

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